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The Extraction and Purification of Radium, Uranium, and Vanadium From Carnotite Ore

THE EXTRACTION AND PURIFICATION OF RADIUM, URANIUM, AND VA~~R~~NADIUM FROM CARNOTITE ORE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

EUGENE MICHENER STALLINGS

ENTITLED THE EXTRACTION AND PURIFICATION OF RADIUM, URANIUM

AND VANADIUM FROM CARNOTITE ORE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

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THE EXTRACTION AND PURIFICATION
of
RADIUM, URANIUM, AND VANADIUM
from
CARNOTITE ORE

* * * * * * * * * * * * * * *

I

Introduction

Ever since the discovery of radium by Mme. Curie and the announcement of its wonderful properties, there has been a great demand for this element. On account of its scientific interest, such extensive investigations have been carried out that the supply of radium at all times has fallen short of the demand. The more recent claim that it has a therapeutic value in the treatment of such diseases as cancer has so greatly increased the demand that the study of radium-producing ores, along with the best methods of extracting the radioactive material, has become extremely important. In view of these facts, it can readily be seen that the demand for radium will be on the increase and that any research which will point out efficient and practical methods for the recovery of this element will be of both scientific and practical value.

This paper presents the results of an investigation, carried out under the direction of Professor B. S. Hopkins, of the various methods of treating carnotite, with the object of extracting not only the radioactive constituents but also the uranium and vanadium which it contains. It has been established by McCoy[1], Boltwood[2], and Strutt[3] that there is a constant ratio between uranium and radium in ores. Consequently the ores richest in uranium con-

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tain the most radium. Among the most important of these ores are pitchblende, autenite, chalcocite, and carnotite. Of these, until recently, pitchblende has been looked upon as the best source of uranium, the mineral usually containing from 40% to 90% of uranaso-uranic oxide, U_3O_8. The great demand for the radioactive elements, however, has nearly exhausted the known deposits of this ore.

The main source of supply for uranium at the present time is carnotite. It is a hydrated vanadate of uranium and potassium[4], and usually occurs as a canary-yellow powder disseminated in sandstone. It does not occur as a rule in a pure state, but as a mixture of minerals containing--in addition to uranium, vanadium, and potassium--varying amounts of silica associated with such elements as barium, calcium, and iron. The principal carnotite deposits are those of Colorado and Utah, where uranium ore is found in far larger quantity than in any other region in the world.

Many of the commercial methods proposed for treating uranium ores, or ores containing both uranium and vanadium, have had as their object the extraction of these elements only, without reference to the recovery of radium. In such cases, the radium has been lost because operators have not known the best methods for obtaining it. A considerable amount of American carnotite has been shipped to Europe. These ores have been purchased mainly for their radium content, and the profit has come largely in connection with the extraction of radium. Moore and Kithil[5], Siegfried Fischer[6], and Parsons, Moore, Lind, and Schaffer[7] have discussed quite fully the principal methods now in use for treating carnotite.

The different methods used may be classified under three general heads, as follows: (1) Use of an acid leach; (2) use of an alkaline leach, followed by an acid leach; (3) fusing the ore with

some material that will break up the ore and make the extraction of the valuable contents possible. Of the first methods may be mentioned Fleck's[8] method, which consists of leaching the ore with dilute sulfuric acid; and that of Moore and Kithil[9], who effect a partial solution by treatment with boiling nitric acid. McCoy's[10] method involves the mixing of the ore with sulfuric acid to form a mud and roasting to a temperature of 300°C or above.

Among those of the second class of methods may be mentioned: Bleeker's[11] process, which consists of boiling with sodium carbonate and leaching the residue with dilute acid; the Haynes-Engle[12] process, which also leaches with an alkaline carbonate; and Fischer's[13] process of evaporating with a sodium hydroxide solution, and roasting.

The most important of the last group of methods are: That used by the Austrian government which consists of fusing the ore with sodium sulfate, which method is well described by Haitinger and Ulrich[14]; and that of Radcliffe[15], who fuses the ore with sodium acid sulfate.

II

Historical

It will not be out of place at this point to say a few words concerning the history of the ore and the elements involved. Carnotite is probably an alteration product of pitchblende, and was discovered[16] by Charles Poulot late in 1887 or early in 1888, in the Rock Creek district of western Montrose County, Colorado. It was named after the President of France at that time. The ore was treated in such a manner as to produce a crude form of the combined oxides of uranium and vanadium, and shipped to France. There the vanadium was extracted and used in southern France for coloring fine

silks, while the uranium content was used in tinting porcelains, glass, etc. Originally all of the carnotite was worked principally for the vanadium content of the ore, but in 1910 Mr. T. F. V. Curran induced the radium makers in England, France, and Germany to experiment earnestly with carnotite, and a strong and steady demand for it was soon developed.

Pitchblende was formerly believed to be an ore of zinc or iron, while by others it was thought to contain tungsten. Klaprath in 1789 was the first to point out the existence in the mineral of uranium. Until 1842, it was thought that he had obtained the metal, but in that year Peligot proved this body to be an oxide, and isolated the metal. Pure uranium has a white color and takes a high polish; it has a specific gravity of 18.7 at 14°; in the powdered state it oxidizes on exposure to the air and decomposes water slowly at the ordinary temperature, but more quickly at the boiling point. Metallic uranium and its compounds are radioactive, which fact was discovered in 1896 by Becquerel. Its principal oxide is U_3O_8, which contains 84.85% uranium and has a specific gravity of 7.193.

In 1801, Del Rio pointed out the existence of a new metal in a lead ore found at Zimapan in Mexico, and gave it the name of Erythronium, from the fact that its salts became red when heated with acids. In 1805, Collet-Descotils expressed his opinion that this supposed new metal was an impure oxide of chromium, and Del Rio accepted this conclusion. In 1830, Sefström described a new metal which he found in the iron of Taberg, and proposed for it the name vanadium. In the same year Wöhler showed that Del Rio's discovery was a true one, and that the Zimapan ore was a vanadate of lead. Sefström, being unable to investigate further the metal, gave the materials to Berzelius and in 1831 this chemist published his re-

sults describing a large number of vanadium compounds. His view was universally accepted until 1867, when Roscoe showed that the substance isolated by Berzelius was either an oxide or a nitride. Metallic vanadium is a light grayish colored powder, has a hardness greater than that of steel or quartz, and takes a splendid polish. It does not decompose water at the ordinary temperature. Its specific gravity is 5.5 at 15°. It is not attacked by hydrochloric acid either when hot or cold, but when heated for some time with strong acid it slowly dissolves. Nitric acid of all strengths oxidizes it with a violence evolving nitrous fumes and forming a blue liquid. The most important oxide is V_2O_5, red rhombic prisms, specific gravity 3.35, soluble in 1000 parts of water.

After the discovery of the radioactive properties of uranium by H. Becquerel in 1896, it was noted that some minerals of uranium such as pitchblende were more active than the element itself, and this suggested that such minerals contained small amounts of some unknown substance possessing radioactive properties in a very high degree. Madame Skladowska Curie, at the suggestion of Becquerel, now undertook the chemical examination of pitchblende in order to find this especially active component. The first material which showed the property in a higher degree than uranium was a substance resembling bismuth, to which Mme. Curie gave the name of polonium in honor of her native country. It has not even yet been obtained in a state of purity. A little later she discovered among the alkaline earths a new element which possessed the property of radioactivity in an especially high degree. It closely resembled barium, but could be separated with some difficulty from the latter by the fractional crystallization of certain salts. To this new element was given the name of radium, and its purification was

finally pushed to a point which justified a determination of its atomic weight. This yielded the value of 226 and entitled the new element to a vacant space in the periodic table just below barium, which position is also in harmony with its spectrum and chemical properties.

The properties of radium are remarkable. Its salts are self-luminous, and constantly give off radiations producing effects similar to those of X-rays. It was found that these rays were given off continuously with undiminished energy, and not only were rays emitted but heat--a gram of radium evolving 133 calories per hour. When the character of the radiation was more thoroly studied it was found that three distinct classes of rays could be distinguished. These are spoken of as the alpha, beta, and gamma rays. Of these, the alpha rays are the least penetrating and have the least action upon a photographic plate, while on the other hand they are the most potent in ionizing gases. The gamma rays are the most penetrating and in their character most resemble X-rays. The beta rays, however, are identical with the cathode rays of the Crookes tube, though they have a higher velocity. They carry a negative charge and are deflected by a magnetic field. The gamma rays are not deflected, and the alpha rays but slightly. In the latter case, however, the deflection is in the opposite direction, showing that these carry a positive charge.

Diagram of Steps in Bureau of Mines Method of Radium Extraction

Ore heated with nitric acid

Residue discarded	Acid solution Precipitation of radium-barium sulphate
Radium-barium sulphate	Solution heated with excess of sodium carbonate
Iron-calcium precipitate discarded	Solution partly neutralized Sodium hydroxide added
Sodium uranate	Solution neutralized Ferrous sulphate added
Iron vanadate	Solution evaporated
	Sodium nitrate
	Nitric acid

Radium-barium sulphate
reduced with carbon

Radium-barium sulphide
treated with hydrochloric
acid

Radium-barium chloride
fractional crystallization

Barium chloride	Radium chloride

III

Experimental Work

The ore used in these experiments was ore from the vicinity of Placerville, Colorado. It was rather dark in color, and was very finely ground, so that practically all of it passed thru a 100-mesh sieve. The ore contained approximately 2.5% V_2O_5 and 1.25% U_3O_8, as determined by the Bureau of Mines method[17].

After looking into the various processes used in the extraction of uranium, vanadium, and radium from carnotite, it was decided to investigate further the method used by the Bureau of Mines which is clearly shown by the accompanying diagram. At first a small sample, 50 grams, was run thru the analysis, but it was found that very unsatisfactory results were obtained. Practically nothing checked with the results obtained by the Bureau of Mines. After working upon a 500-gram sample and also obtaining poor results, work was started upon a sample of about 15,000 grams, for it was believed that the results would coincide more closely by using this amount, since the Bureau of Mines report was based on the results obtained by using very large samples.

The ore, ground to 100-mesh, was leached with strong hot nitric acid. The amount of acid used was 100 grams of 100% HNO_3 to 500 grams of ore, the acid being diluted to about 38% strength. However, the strength may be varied somewhat, for ores high in sulfates require stronger acids. The addition of a small amount of hydrochloric acid to the nitric acid increases the solvent action. Therefore, if the nitric acid does not contain hydrochloric acid, enough hydrochloric acid may be added to make the proportion of concentrated hydrochloric acid to 100% nitric acid, about 2.5%. The acid was brought near the boiling point by passing in live steam,

and the ore was then run in and stirred during the process.

Nitric acid is not a very good solvent of vanadium, although it readily breaks up the vanadium minerals. If too much vanadium is present, there is a tendency for vanadic acid to separate out in the acid as a reddish-brown precipitate. As this is rather gummy, it retards filtration. If considerable vanadium separates in this manner, filtration may be so retarded that the acid cools down, causing a considerable loss of radium by reprecipitation. If there is little or no separation of vanadium in the acid, filtration takes place readily and quickly, and the extraction of radium is thereby increased. Therefore, if the heating is continued with the object of decomposing other vanadium minerals, which may be present, there is likely to be a loss of radium. Consequently, it is better not to continue the heating too long, but to make the extraction of radium the main object. The uranium is practically all dissolved under the conditions mentioned.

The solution was then decanted thru a vacuum filter, and the sand washed with 10% nitric acid. After the acid leach had gone thru the filter, the acid wash with the remainder of the ore was dumped on the filter and given a thorough washing with hot distilled water. The residue was discarded and the filtrate run into a large earthenware jar. Sodium hydroxide solution was then run in slowly, the solution being stirred continuously. After a certain amount of sodium hydroxide had been added, a greenish precipitate appeared, and as more alkali was added this precipitate got heavy, and finally tended to turn slightly brown. At this stage the addition of the alkali was stopped, for the object was to reach as nearly as possible the neutral point without forming a permanent precipitate. If too much alkali were added, iron and vanadium would be precipitated,

while if not enough is added the acidity remains too high, and the solvent action of the nitric acid on the radium-barium sulfate precipitate would not be sufficiently decreased.

About twenty grams of barium chloride was then added, and after the liquid was thoroly stirred, sulfuric acid was slowly added, stirring continued for one hour, and then the solution allowed to settle over night. The sulfuric acid not only precipitates radium-barium sulfate, but also dissolves the small precipitate of iron and vanadium in the solution. Consequently the final precipitate obtained was a fairly clean one of radium-barium sulfate, containing only small traces of iron and vanadium. By means of a siphon the clear solution was decanted into a jar containing an excess of boiling sodium carbonate, where the iron, calcium and aluminium were precipitated, and the uranium and vanadium went into solution as the double carbonate of uranium and sodium, and as sodium vanadate. As long as the alkali is in excess, there is little chance of the solution boiling over; should the neutralization point be nearly reached, there is serious danger of such boiling. The liquid was heated during the addition of the acid and maintained at a temperature near the boiling point during the entire period. This is important because otherwise the precipitate, which should be red, becomes brown or even bluish-brown and carries considerable vanadium and too much uranium.

The radium-barium sulfates and the associated liquor were then conveyed to a suction filter, filtered, washed, and finally treated with a dilute solution of sodium hydroxide in order to remove the last traces of free acid. The radium-barium sulfate was then carefully scraped from the filter paper, placed in a shallow porcelain dish and dried in a hot air oven. It was then treated as

will be described in subsequent pages.

The filtrate from the iron precipitate carries the uranium in solution as a double sodium uranyl carbonate and the vanadium as sodium vanadate. The solution was partly neutralized with nitric acid, the acid being added until a yellow precipitate begins to form. This precipitate is supposed to be uranyl carbonate, but in reality it contains more sodium uranate than uranyl carbonate, as on ignition it gives a very small amount of oxide. If too much acid is added at this stage the amount of vanadium that appears with sodium uranate is considerably increased. When the precipitate began to form the addition of acid was stopped and sodium hydroxide was added to the hot liquor until the uranium was completely precipitated as sodium uranate. After the addition of the sodium hydroxide and precipitation of the uranium the solution was boiled for about an hour in order to promote complete precipitation, and then filtered and washed. As the sodium uranate requires re-treatment, owing to the fact that it carries vanadium, it is not necessary to wash the cake as completely as might otherwise be required. It was found practically impossible to obtain a precipitate that did not carry considerable quantities of vanadium, most of which appears probably as uranium vanadate.

The filtrate from the sodium uranate precipitate contained the vanadium as sodium vanadate. The solution was brought to the boiling point and just neutralized with nitric acid, the boiling being continued long enough to eliminate carbon dioxide. A solution of ferrous sulfate was then run into the hot solution, agitation being accomplished by means of compressed air. The heating of the solution was stopped before the addition of the ferrous sulfate, for if heating is continued longer a complete precipitation of the va-

nadium is not obtained. It is advisable to have the solution just neutral after the addition of the sulfate, and if it is neutral before this addition it will be slightly acid afterwards. It was found convenient to make the solution exactly neutral before the addition of the ferrous sulfate and then to add a few grams of sodium hydroxide to neutralize the solution once more after the addition of the ferrous sulfate. In this way, practically all of the vanadium is precipitated as iron vanadate, only a mere trace going through in the filtrate. The precipitate is probably a mixture of the different vanadates of iron, and has a greenish black color.

As has already been stated, most of the sodium uranate that was obtained contained some vanadium. It has been found impossible to precipitate sodium uranate in alkaline solution containing both uranium and vanadium, and not to precipitate at the same time a considerable amount of vanadium with the uranium. As uranium should be as free as possible from vanadium, the economical refining of uranium is important. Smith and Gibbs[18] have shown that vanadic acid can be removed from heated sodium uranate by means of hydrogen chloride, the vanadium volatilizing. Hillebrand[19] has shown that vanadium can also be removed from ores in the same manner. In the case of sodium uranate, the product left behind is probably a mixture of sodium chloride, uranyl chloride, and sodium uranate. However, it was found that vanadium could be separated from uranium quite efficiently by a fusion method. The sodium uranate was heated with two and one-half times its weight of sodium sulfate until the whole mass was fused. It was found advisable to add a small amount of sodium nitrate to the sulfate in order to lower the melting point. The product of this fusion was broken up and leached, and practically

all of the vanadium went into solution while the uranium remained the same.

The radium-barium sulfates, after being thoroly dried, were ground and mixed with about one-fifth their weight of powdered charcoal. This mixture was then charged into a graphite or an alundum lined fireclay crucible and placed in a small gas furnace for nine or ten hours, at a temperature of about 850°C. Reduction takes place readily according to the equation

$$BaSO_4 + 4C = BaS + 4CO$$

the CO burning at the top of the furnace. It was found that the graphite crucibles were badly attacked, so upon subsequent reductions an ordinary fireclay crucible with a lining of alundum cement was used, and found to be much more satisfactory. When the evolution of carbon monoxide had stopped, the crucible was allowed to cool and the radium-barium sulfide removed and broken up. Under such conditions it was usually possible to get an 80-85% reduction. The sulfide was then dissolved in dilute chemically pure hydrochloric acid. The residue obtained upon filtration consists of undecomposed radium-barium sulfate, a small amount of charcoal, and some silica. This residue was charged with the next batch of radium-barium sulfate. The filtrate was then run into a large porcelain dish and evaporated to dryness. The crystals were dissolved in water and so concentrated that upon cooling about one-half of the barium chloride crystallized out. The liquor was siphoned into another evaporating dish to the right, and the process repeated. Thus by moving the crystals from right to left and by moving the mother liquor from left to right a chloride may be obtained that is much richer in radium than the original substance. The crystallization factor of the hydrochloric

acid solution was about 1.5 to 1.6; that is to say, if 50% of the barium chloride were removed, there would be 50% more radium in the crystals removed than in the liquor left behind. This, of course, is due to the greater insolubility of the radium than of the barium. In consequence, the crystal fractions are progressively enriched with radium, and the mother liquor fractions are progressively impoverished, as the number of crystallizations increases. The salts of most metals, such as iron, aluminium, and vanadium, that may occur with the radium-barium salt as impurities, pass into the mother liquors, and give no difficulty in the enriching radium fractions.

It was at first hoped to be able to make some radium measurements, but owing to the low-grade ore with which the writer had to work, this was found to be practically impossible. The crystal fraction containing the highest percentage of radium was removed and dried. This was then so placed as to expose a photographic plate to the action of the radioactivity of the rays emitted. In order to do this effectively, a plate was placed in a black X-ray plate envelope and carefully sealed so that no other source of light could affect it. This plate was then covered with a sheet of lead which had a slit cut in it, and the slit covered with the radium-barium chloride. Different plates were exposed to the action of the rays for 24, 36, and 48 hours. No results could be seen upon the plates exposed for 24 or 36 hours, but upon the plate which was exposed for 48 hours a very faint spot could be seen, which gives indication of some radioactive substance. Owing to the lack of further time it was impossible to continue the radium measurements, but it is believed that if further time could have been had, in order to bring about a bromide fractional crystallization, and time for longer exposures, very satisfactory results could have been obtained.

IV

Conclusion

It was found that this method of extraction was not entirely satisfactory, for a number of reasons. In the first place it was practically impossible to get all of the valuable constituents into solution by simply using an acid leach. The nitric acid oxidized considerable vanadium to such a form that it was insoluble, and this could be removed only by re-treating the residue with an alkaline carbonate. This is no doubt due to the grade of ore with which I had to work, for it was not a pure carnotite. A qualitative analysis showed the presence of calcium, aluminium, lead, iron, and zinc in addition to uranium and vanadium. It is a well-known fact that the presence of various elements greatly affects the behavior of uranium, and especially vanadium. Friedel and Cumenge[20], after having extracted the vanadium by using dilute nitric acid were able to separate the vanadium in the filtrate from other ingredients by evaporating to dryness. Under these conditions, they claim, the vanadium, in excess of nitric acid, becomes insoluble upon evaporation and can be separated quantitatively from uranium, whose nitrate is soluble in water. Hillebrand[21], however, in using this method of Fiedel and Cumenge on some complex ores, found that he could not always get a perfect separation, because it was impossible for him, first, to prevent a little of the vanadium going into solution with the uranium and,, second, to prevent small amounts of the uranium being retained with the vanadium. Moore and Kithil state that they were able to decompose pure carnotite, and even such vanadiferous silicates as roscoelite by boiling them for an hour with concentrated acids. With the ore used in this work, which is the kind that

constitutes the bulk of material available in America for technical purposes, acid did not seem to bring the vanadium completely into solution. Other reasons that this process of extraction was not satisfactory are that as a general thing the reagents used were far too small to insure completion of the reaction in which they were involved and the fact that, upon a commercial scale, the expense involved would be practically prohibitive. The most rigid economy would have to be used in the recovery of as many reagents as possible. This, no doubt, is the reason that the amount of reagents used is often less than the theoretical amount, for the loss due to incomplete reaction may be less than the cost of a few additional units of the reagent.

In order to remedy some of these defects a more complete study of other methods should be made. It seems to me that the most promising would be in first removing the uranium and vanadium by means of an alkaline leach or fusion, and then treating the residue with acid in order to remove the radioactive constituents. In this way one should be able to produce an efficient method for the extraction of radium, uranium and vanadium which would be much less expensive, and more applicable to commercial uses, than the present method.

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